

Morphology and Characterization of Conductive Films Based on Polyaniline-Coated Polystyrene Latexes

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ABSTRACT: The polyaniline (PANI)-coated polystyrene (PS) latexes were synthesized, and the electrically conductive films were prepared thereafter. The weight ratio of PANI was 5%. Thermal analysis of the latices was performed using DSC and TGA. In this study, the electrically conductive films were prepared above the PS glass transition temperature (T_g). During the film formation, the effects of the annealing temperature and atmosphere (air or N_2) on the film resistance were investigated. In addition, the film morphology was

observed utilizing scanning electron microscopy. The film resistance decreased in the initial heating stage due to the increasing temperature and the compaction of film. Then the film resistance increased with further annealing due to the aging of PANI. Typically, the film resistance was about 6000 Ω /sq, and the conductivity was 0.3 S/cm. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5406–5413, 2006

Key words: latex; polyaniline; polystyrene; film formation

INTRODUCTION

In recent years, intrinsically conductive polymers (ICPs) have been widely studied and developed because of their variable conductivity (10^{-12} – 10^3 S/cm)^{1–3} and properties of organic polymer, which have led to applications in various fields: traditional industries, optoelectronics, biochemistry, and so on. Among all conductive polymers, it has been proven that polyaniline (PANI) has more advantages, such as better environmental stability and lower cost. However, some disadvantages, such as stiff structure, brittle mechanical property, and insolubility in common solvents, limit the processing and the application of PANI.

Several researchers have studied the preparation of core-shell latex particles with conducting polymer shells.^{4–10} The approach demonstrated better processability, and the continuous conductive polymer layer could lead to relatively high conductivity even at very low conducting polymer loadings. Okubo et al.⁴ synthesized micron-sized conducting polystyrene-polyaniline (PS-PANI) core-shell particles with polyvinyl alcohol (PVA) and showed that the conductivity was

much larger than the PS/PANI particles blends. Barthelet et al.⁵ reported that the PS latexes with 1.6 μ m in diameter could be coated with PANI layers using poly(*N*-vinylpyrrolidone) (PVP) stabilizer; the PANI-coated PS particles performed a nonuniform morphology, compared to the polypyrrole (PPy)-coated particles by Lascelles et al.⁶ The film-forming latex particles poly(*n*-butyl methacrylate) (PBMA)/PPy were prepared by Huijs et al.^{7–10} PBMA latex has a low film-forming temperature that is around ambient temperature. However, the high T_g materials such as PS and poly(methyl methacrylate) (PMMA) latex are nonfilm-forming under the ambient temperature. Thus, the core-shell latex films are prepared by heating above the T_g of core materials.

The film formation of the latices has been reviewed by Dobler and Holl, Winnik, Keddie, and Meincken and Sanderson.¹¹ The film formation process for latices is described in three stages: water drying, particles coalescence, and particle interdiffusion. First, water evaporates rapidly from the surface, and subsequently the interstitial water diffuses out slowly. In the evaporation stage, the particles are drawn to ordered areas. If the annealing temperature is higher than T_g of the latices, the latex forms an ordered array and the surface flattens. The particle boundaries are deformed into hexagons and the adjacent particles coalesce to each other. Furthermore, the segments of polymer chains diffuse from one latex particle to another, which enables the formation of a continuous film and enhances the mechanical property.

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The objective of this study is to prepare flexible and conductive films based on PANI-coated PS latex particles to strengthen the mechanical property without severely decreasing the conductivity and thus extend the applications of PANI. PS is used to enhance the mechanical strength. Moreover, it could reduce the amount of the high-cost and toxic aniline monomers, which provides benefits in the commercial production. However, the film formation of PANI-coated PS particles is different from that of usual polymers because solvent-casting methods are not feasible. Most solvents that dissolve PANI would also dissolve PS, and it might result in phase separation between the two polymers and a drop in conductivity. Here we report an effective method of preparing films with relatively good conductivity: heating the latex particles above the T_g of PS. Since the degradation of conductivity occurs at high temperature, it is important to reduce the film formation time. To achieve this, we investigate the change of the film morphology during the film formation and the relations between the film resistance and the conditions of the film formation.

EXPERIMENTAL

Materials

All solvents and chemicals were of reagent quality and were used as received unless otherwise stated. Sodium hydroxide was purchased from Showa (Tokyo, Japan). Styrene monomers (Acros, Geel, Belgium) were purified by washing with 0.1N NaOH repeatedly and then washed with deionized water until pH = 7. Azobis(isobutylamide hydrochloride) (AIBA), sodium dodecyl sulfate (SDS), aniline, and ammonium persulfate (APS) were obtained from Acros. Tetrahydrofuran (THF) and hydrochloric acid solution were obtained from Tedia (Ohio, USA) and Scharlau (Barcelona, Spain), respectively.

PS latex synthesis

PS latex particles were synthesized utilizing emulsifier-free batch method. Styrene (40 mL) was added in the deionized water (720 mL) in a four-necked reaction vessel fitted with a condenser and a stirrer (300 rpm) and purged with nitrogen. After the reaction vessel was heated to 70°C, a preheated initiator solution containing 1.3 g AIBA was added. The PS polymerization was allowed to proceed for 24 h. PS particles were then purified by repeated centrifugation and redispersion cycles.

PANI coating protocol

The PANI-coated PS latex particles used in this study were synthesized with a multi-step emulsion polymerization process with SDS as a surfactant according

to the previous study.¹² PS latex (solid: 0.3 g) was diluted with deionized water to a total volume of 25 mL, and the anionic surfactant SDS (0.07 g) was added. The solution was then stirred at 0–5°C for 12 h to allow the attainment of adsorption–desorption equilibration. Aniline (aniline/PS = 5 wt %) dissolved in the HCl aqueous solution was added and stirred for 1 h, followed by the addition of aqueous APS solution (APS/aniline = 1.25 mol ratio) to start the reaction. The polymerization proceeded at 0–5°C for 6 h and then at room temperature for another 18 h. The PANI-coated PS particles used in this study were made by several batches. Then particles were mixed together to make sure particles used for each sample were same.

Film preparation

The PANI-coated PS latex solution was spread onto the PET substrate and dried at room temperature, which resulted in dry particle stacks. Then they were put into a vacuum oven at room temperature to remove the residual water. The film was prepared by increasing the temperature. Influences of the temperature and the atmosphere (air or N₂) on film formation were investigated.

Measurements

Fourier transform infrared spectroscopy

The FTIR spectrum of PANI-coated PS particles was recorded with a Jasco FT/IR-480 Plus spectrometer (Tokyo, Japan) using the KBr pellet technique.

Scanning electron microscopy and transmission electron microscopy

The size and surface morphology of the latex particles were observed utilizing SEM (JEOL JSM-6300 and Hitachi S-800; Tokyo, Japan) operating at 15 and 20 kV, respectively. Also, the morphology of the conductive film was studied with SEM. SEM samples were mounted on a double-sided adhesive carbon disk and sputter-coated with a thin layer of gold to prevent sample charging problems. TEM images were obtained using a Hitachi H-7100 transmission electron microscope.

Thermogravimetric analysis and differential scanning calorimetry

To remove the residual water of latex samples before the thermal analyses, latex samples were first heated to 50°C and then held for 24 h in a vacuum oven. The thermal weight decomposition of latex particles was examined by TGA (TA instruments TGA 51) at a heating rate of 10°C/min to 500°C. Thermal transitions were measured utilizing DSC (TA instruments DSC

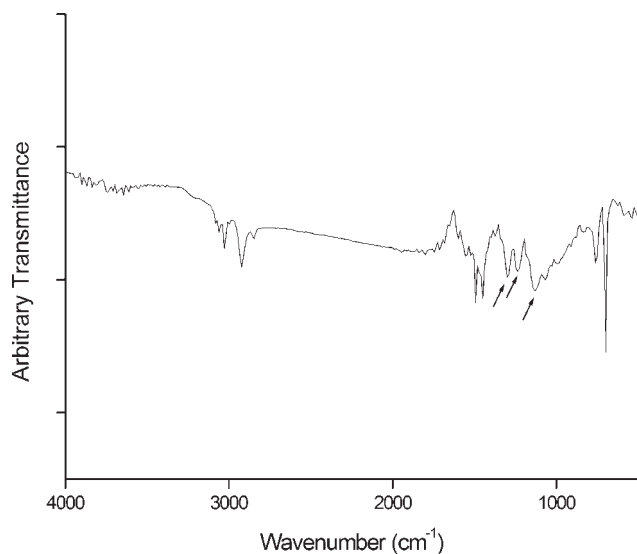


Figure 1 FTIR spectrum of PANI-coated PS particles. Arrows indicate absorption bands attributed to PANI.

2010; Delaware, USA) at a heating rate of 10°C/min to 150°C, and T_g of PS could be determined. All the measurements were under nitrogen atmosphere.

Electrical resistance measurements

The resistance of compressed pellets of the dried PANI-coated PS latices was determined using standard four-point probe techniques at room temperature. The both sides of the pellet were sputter-coated with thin layers of gold to prevent the influence of contact resistance. The resistance measurement of the conductive films was conducted by placing the films on a hot stage (Linkam THMS 600; Surrey, UK) with gold wires connecting the electrodes on the films and an ohmmeter, which enabled resistance readings to be recorded as a function of time at different temperatures.

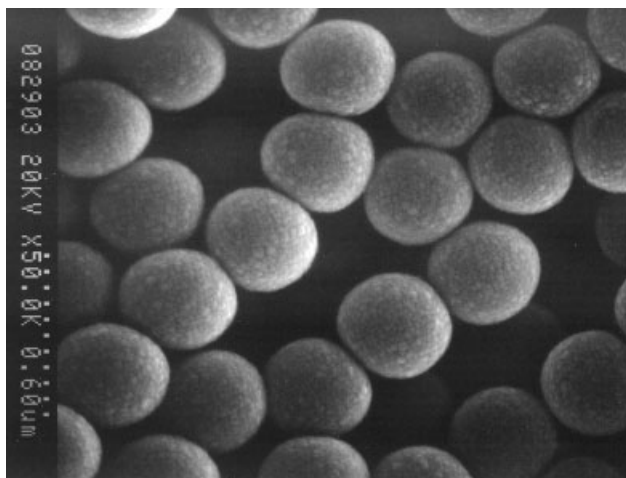


Figure 2 SEM micrograph of cationic polystyrene latex.

RESULTS AND DISCUSSION

Synthesis and analysis of PANI-coated PS latex particles

The synthesis of PANI-coated PS latex particles basically follows Wang's method.¹² In short, an anionic surfactant (SDS) was first adsorbed onto the surface of presynthesized PS latex to aid the adsorption of aniline, and the addition of APS initiated the polymerization of aniline. The FTIR spectrum of PANI-coated PS latices is shown in Figure 1. Three strong absorption bands attributed to PANI were observed around 1300, 1240, and 1140 cm^{-1} , similar to the values reported in the literature,^{5,12} even though the maximum loading of PANI on this latex was only 5 wt %. It indirectly confirmed that PS latex was coated with PANI.¹²

As shown in the scanning electron micrograph (Fig. 2), prepared PS latices had a uniform size of about 400 nm. The particles were suspended stably in water medium due to the NH_2^+ from cationic initiator AIBA dispersing uniformly on the particle surface, which facilitated the PANI coating process. Comparing Figures 2 and 3, one could find that the surface of the latex particles became less uniform after thin layers of PANI were coated on PS latices. It meant that the PANI coating was not uniform in thickness or even incomplete. It is consistent with the results reported by Barthet et al.⁵ The nonuniformity of PANI coating might result in the migration of PS chains out from the thinner part during the later heating procedure, which induced the morphology change of the latices and the film formation.

The morphology of PANI-coated PS particles was also examined by solvent extraction. The dried PANI-coated PS particles on the glass were immersed into the THF solvent to remove PS. This solution was left overnight. The resulting residues were washed gently with THF and dried. The morphology of PANI resi-

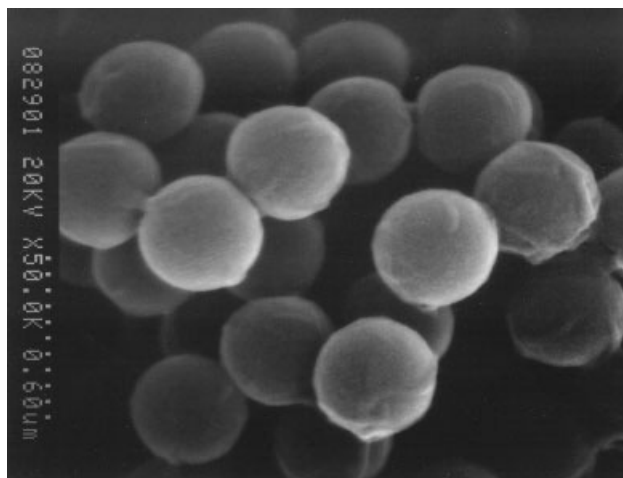


Figure 3 SEM micrograph of PANI-coated PS particles.

dues was examined by SEM. The result is shown in Figure 4. It revealed a "broken egg shell" morphology, which reconfirmed that PS latex was coated with PANI. The thickness of PANI was about 40 nm, thicker than the calculated value due to the nonuniform nature of the coating. If one assumes the coating is complete and uniform, the thickness can be calculated using the following equation

$$l = r \left(\sqrt[3]{\left(\frac{M_2 \rho_1}{M_1 \rho_2} + 1 \right)} - 1 \right)$$

where l is the thickness of the coating, r is the radius of the uncoated latex particles, M_1 and ρ_1 are the mass fraction and density of the PS component, and M_2 and ρ_2 are the mass fraction and density of the PANI component, respectively. The densities of PS and PANI are assumed to be the same as reported by Barthelet et al., 1.05 and 1.40 g/cm³, respectively.⁵ Thus, the calculated thickness is about 5 nm, much less than the measured value.

Figure 5 is a TEM micrograph of PANI-coated PS particles. Nonuniform coatings (indicated by arrows) could be observed, which provided evidence of PS being coated with PANI. However, removing PS yielded only fragments of PANI coatings (similar to those in Fig. 4) but no hollow spheres that were reported in other studies.^{4,13,14} Again, this was probably because of the inhomogeneous nature of the PANI coating.

The thermal behaviors of the dried PS latex particles and PANI-coated PS latex particles were studied by TGA and DSC. The thermogravimetric analysis of the neat PANI salts was reported in the literature.¹⁵ A three-step weight loss process was found, in which water evaporated from the polymer chain up to 110°C, followed by the loss of a small amount of acid

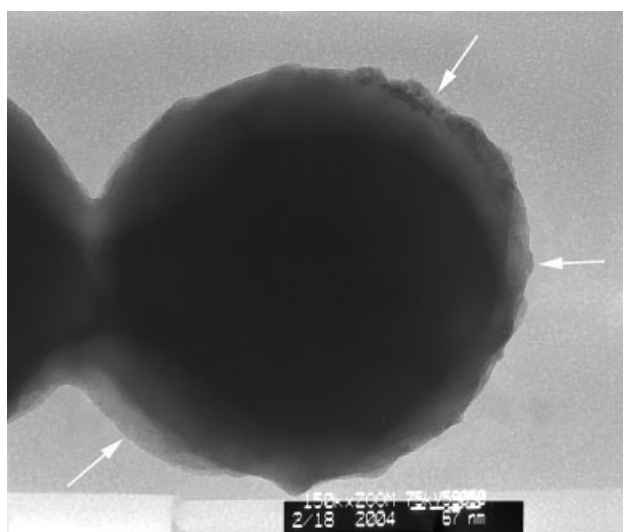


Figure 5 TEM micrograph of PANI-coated PS particles. PANI coatings are indicated by arrows.

as volatile gas, and finally the PANI chain decomposed due to thermal degradation or oxidation. In this study, the thermogravimetric results of neat PS and PANI-coated PS latex particles are shown in Figure 6. There was no weight loss of neat PS latex particles below 270°C. However, a slight weight loss from room temperature to 350°C was observed in PANI-coated PS sample. This result was due to partial acid escaping and water evaporation, which consisted with the previous study. As in the temperature region higher than 400°C, primary weight loss of the PANI-coated PS latex was due to the degradation of PS, because the degradation temperature of PANI should be higher according to the literature. Furthermore, the degradation temperature of PS in PANI-coated PS was higher

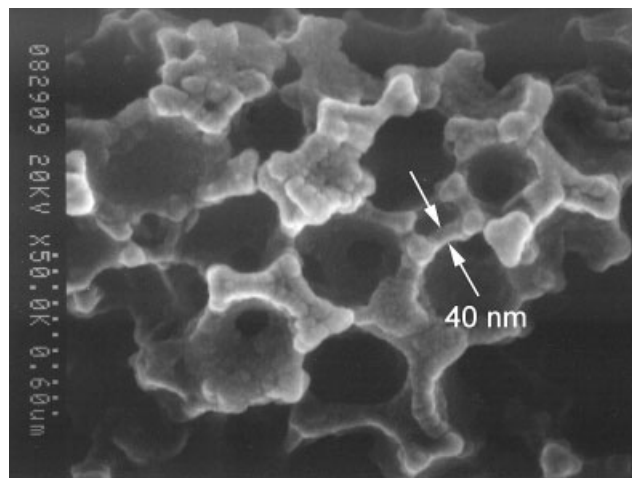


Figure 4 SEM micrograph of the remaining PANI residues, after THF extraction of PANI-coated PS latex.

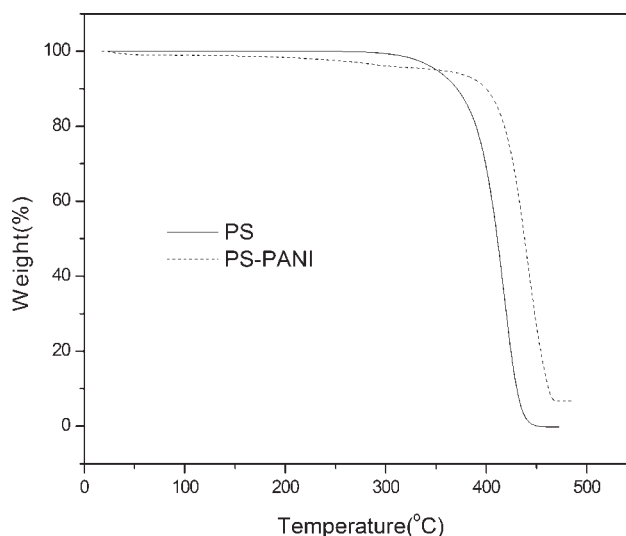


Figure 6 TGA curves of the neat PS latex and the PANI-coated PS particles.

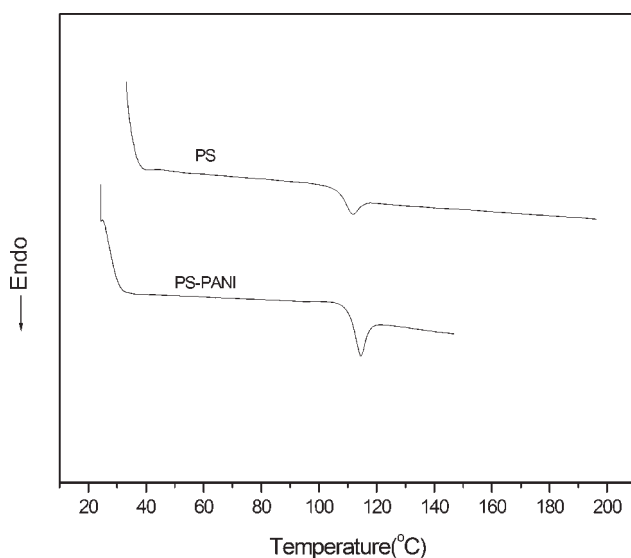


Figure 7 DSC curves of the neat PS latex and the PANI-coated PS particles.

than that of the neat PS latex. The DSC results are shown in Figure 7. The glass transition temperature of PANI-coated PS particles was about 110°C, which was 4°C higher than that of neat PS latex.

The conductivity of the compressed pellet of the PANI-coated PS latex particles was about 0.1–0.01 S/cm. It was lower than the neat conductive PANI salt, whose optimum was 10–100 S/cm. It might be because the order arrays of polymer chains of the neat conductive PANI salt enabled the electrons to transmit along the shortest path. For the latex pellet, however, only PANI coating could provide conductance. Nonconductive PS occupied most of the bulk materials, which prolonged the transmitting path and reduced the actual conduction area. Besides, there were some voids between spherical latex particles. The above factors could result in the lower conductivity of the latex pellet.

Preparation and characterization of PANI-coated PS latex films

In this study, the film formation of PANI-coated PS latex particles was performed at the temperatures that were higher than the T_g of PS. Above the PS T_g , the interdiffusion of the PS polymer chains facilitated the film formation and provide the film mechanical property. Films were pretreated in a vacuum oven for 24 h to remove the residual water inside. The initial conductivities of most films at room temperature before heating procedure were $\sim 10^{-1}$ S/cm. The influences of the annealing temperature, atmosphere, and the morphology change on the film resistance during the film formation were investigated and are discussed below. The decrease of resistance may result from two

major reasons. One is the temperature effect, and the other is the morphology change, vanishment of voids, and increase in contact area.

The influence of the annealing temperature

Samples were heated on the hot stage at a heating rate of 20°C/min from room temperature to 120, 130, and 140°C, respectively, and then kept at the annealing temperatures for a day. In the initial heating period, the film resistance decreased sharply with time. After reaching the minimum, the film resistance increased slowly with time. The changes of the relative film resistance with heating time at various annealing temperatures are depicted in Figure 8(a) (R_0 : the film resistance before heating). For the annealing tempera-

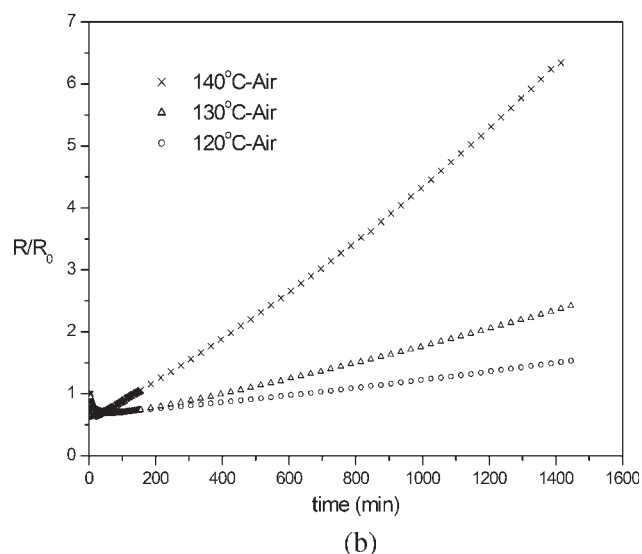
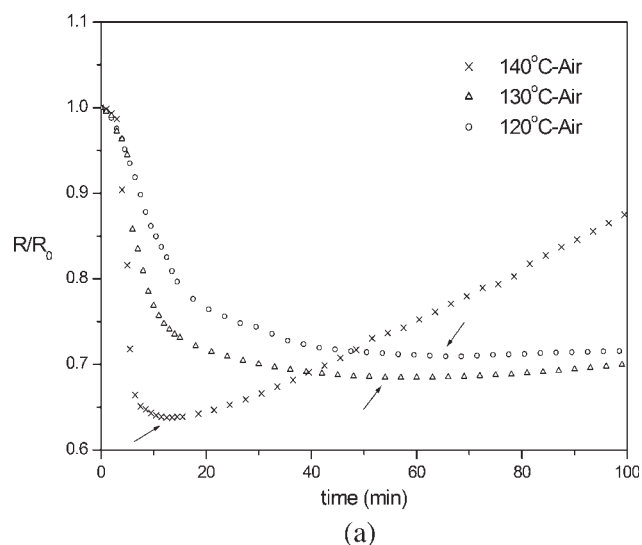


Figure 8 Variation of the relative resistance of the latex films versus heating time at various annealing temperatures; (a) heating for 100 min; (b) heating for 24 h. The minima are indicated by arrows.

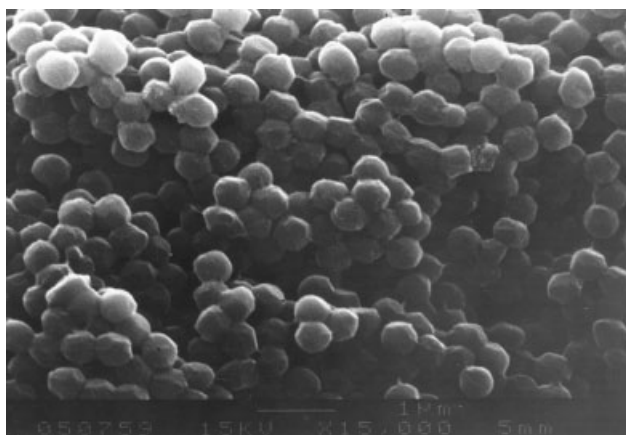


Figure 9 SEM micrograph of the cross section of the latex film heated from room temperature to 120°C at a heating rate of 20°C/min.

ture 120°C, the resistance clearly decreased in the initial 15 min and the minimum value was achieved at about 65 min. Also, it was observed that the latex film changed from opaque to translucent at the minimum resistance. After the resistance-decreasing region, the resistance started to increase with further heating, as shown in Figure 8(b). After heating for 24 h, the resistance was 1.5 times the original value for the annealing temperature 120°C. Similar behaviors were observed for 130 and 140°C. In the resistance-decreasing region, the resistance decreased even more rapidly and greatly with increased annealing temperature and reached the minimum earlier. However, in the resistance-increasing region, the resistance also increased more rapidly and greatly with increased annealing temperature. The change of resistance with annealing time would be discussed below.

The initial resistance decreasing. The initial decrease of resistance was mainly due to temperature increasing from room temperature to the annealing temperature and the compaction of film upon film formation, which was consistent with the previous study.⁹ It was thought that the conductive behavior of PANI was similar to that of semiconductor. The mobility of the charge carriers increases with increasing temperature. Thus, the resistance decreases with increasing temperature. As one would expect, the magnitude of the decrease was strongest for the highest annealing temperature, 140°C. About 10 min after heating from room temperature, the film resistance reached the minimum, and the $(R/R_0)_{140^\circ\text{C}}$ value was about 0.63. To roughly estimate the temperature effect on the decrease of resistance during this period, the film was quenched to 30°C right after the achievement of the minimum resistance, and the relative resistance was measured at 30°C. The $(R/R_0)_{30^\circ\text{C}}$ was about 0.83. It was assumed that the morphology of the film was not changed during the quenching. Therefore, the increas-

ing of (R/R_0) from 0.63 to 0.83 was due to the temperature effect. The other reason for the decrease of resistance was the change of the film morphology. The dry latex particles on the PET substrate were basically spherical before heating, as shown in Figure 3. It was observed on the film surface that the spherical particles gradually flattened when they were heated on the hot stage from room temperature to 120°C. Some of the adjacent particles deformed and the contact surface area increased. In Figure 9, the cross section of the film obviously showed that the packed and compressed particles deformed to be multilateral and coalesced with the adjacent particles. Also, partial voids inside the film disappeared gradually, and thus the film became more compact. Furthermore, when the temperature reached 140°C, the particles flattened completely and boundaries between particles vanished, as shown in Figure 10. At 140°C, PS was a viscous melt already while PANI was still in solid state. The movable PS flowing between latex particles facilitated the compaction of film to reduce the film resistance due to easier hopping of charge carriers between the PANI coatings. The higher the annealing temperature was, the easier the flow of PS was, and so was the film formation. Therefore, the resistance decreased more rapidly and greatly with increased annealing temperature and reached the minimum earlier.

The later resistance increasing. The reason that the later film resistance increased with the heating time was the thermal aging of the conductive PANI, especially at high temperature, including the loss of doping acid (HCl) and the chemical reactions inside the film, such as oxidation, hydrolysis, chlorination of the aniline rings, or chemical crosslinking of the PANI. Studies^{16–18} about the thermal behaviors of the conductive PANI reported that a small part of the doping acid would escape from the polymer chain above 100°C. However, such a rare amount of dedoping was not

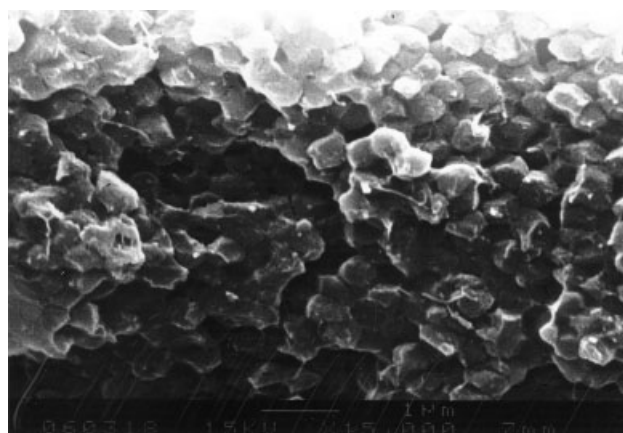


Figure 10 SEM micrograph of the cross section of the latex film heated from room temperature to 140°C at a heating rate of 20°C/min.

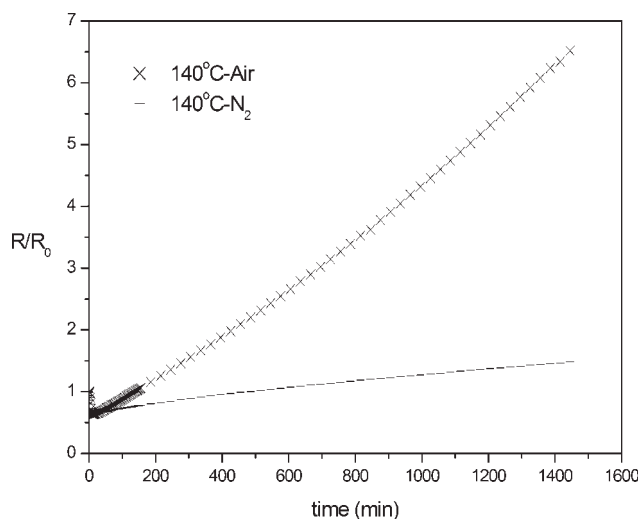


Figure 11 Comparison of the relative resistance of films annealed in the air and in the N_2 .

adequate to exhibit a great increase in resistance. It was reported that in the unaged sample, most of the chlorines existed as Cl^- ions forming ionic bonds with polymer chains and therefore participating to the doped state of the system. Some of them transferred into covalent bond after aging at high temperature and participated the chlorination of the aniline rings. The conductivity degradation or chemical structure changes of conductive polymer were seriously influenced by the oxygen when exposed in the air at high temperature. As Figure 11 shows, the existence of oxygen greatly increased the film resistance during annealing. After heating for 24 h at $140^\circ C$, the resistance increased to more than six times in the air but only slightly increased in the N_2 . This marked difference mainly resulted from the oxidation and hydrolysis of PANI with the oxygen and water in the air. These reactions created defects inside the polymer chain to reduce the conductivity. However, film resistance still increased with heating time in the N_2 . This resulted from the escaping of the partial doping acid from the PANI and the chemical crosslinking of the polymer chains. The later reaction seriously hindered the transmitting path at high temperature.

Morphology change of the film formation

This study observed the morphology change of the film surface and cross section by SEM. As mentioned before, the shape of particles flattened, the voids disappeared, the particles coalesced, and PS flowed out of the particles to form the film in the initial heating. Figure 12 is the SEM micrograph of the cross section of the film heated for about 10 min at $140^\circ C$. The particle outlines vanished due to the migration of PS chain to form a continuous film. Several aggregations of PS dispersed on the film surface. As shown in Figure 13,

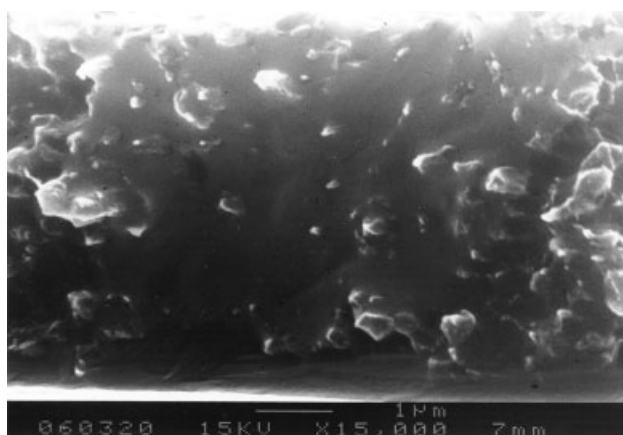
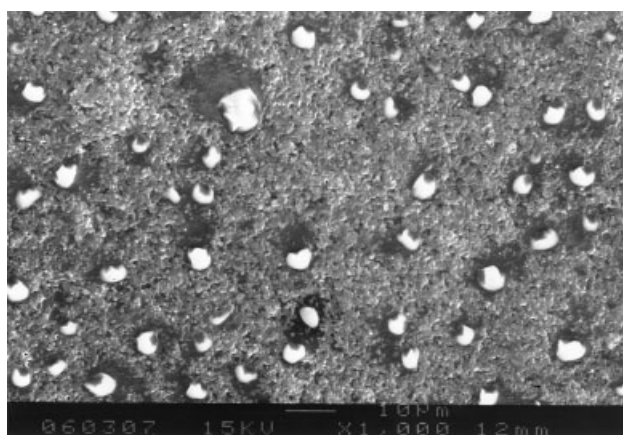
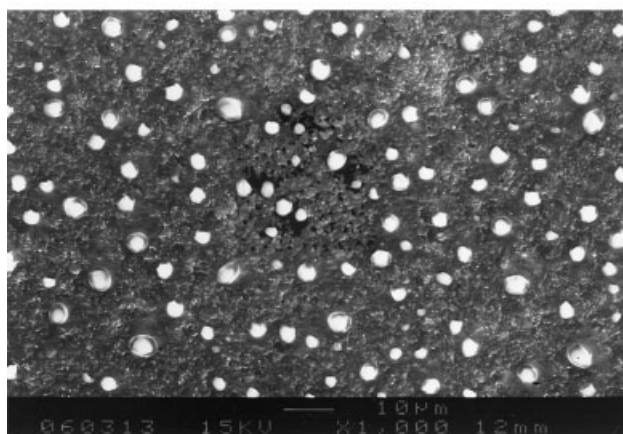


Figure 12 SEM micrograph of the cross section of the latex film heated at $140^\circ C$ for 10 min (with the minimum resistance).

the amount of the aggregated PS (appears as white particles) on the surface increased with the heating time. The above film formation procedures could also



(a)



(b)

Figure 13 SEM micrographs of latex film annealed at $140^\circ C$; (a) for 10 min (with the minimum resistance); (b) for 35 min.

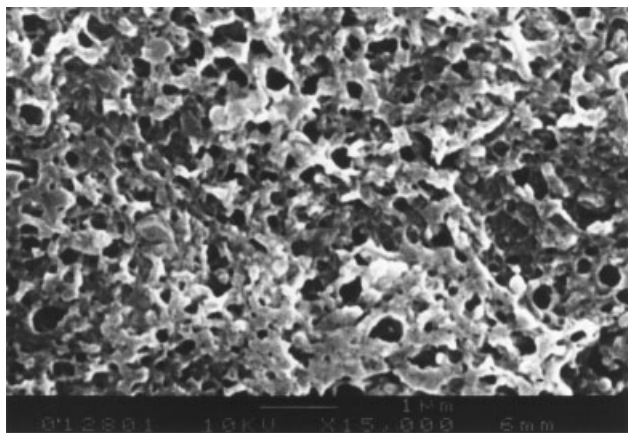


Figure 14 SEM micrograph of latex film annealed at 140°C for 35 min after THF extraction.

be observed at a lower temperature. However, it took more time. To observe the PANI part and identify whether the aggregations on the film surface were PS or not, the heated film was immersed into THF. One could find that the aggregations on the film surface disappeared after THF extraction, and the film morphology changed from dense film to broken egg shells with the approximate dimension order corresponding to the PANI coatings (Fig. 14). Because the annealing temperature was not high enough to cause the melting of PANI, it was believed that PANI might not be able to cover the whole PS particles completely and let the PS chain to migrate out of the PANI coating to induce PANI to collapse.⁵ Therefore, the morphology of the conductive film was like that many broken egg shells dispersed in PS and connected with one another. The aggregation of PS on the film surface was due to the sufficiently large thermodynamic incompatibility and the interfacial tension between PS and PANI. Besides, PANI was in the glassy state, and only PS chain could flow and aggregate on the film surface at the annealing temperature.

CONCLUSIONS

This study has synthesized PANI-coated PS latices by the adsorption of SDS. Compared to the neat PS latex, the primary weight loss temperature and glass transition temperature of the PANI-coated PS particles slightly shifted to high temperature region. Moreover,

the PANI-coated PS latex films were successfully prepared by a multi-step procedure: drying, particle-coalescence with heating above the PS T_g , and PS chain migration to facilitate the film formation to enhance the mechanical property. In the initial heating, the film resistance decreased due to the temperature effect and particle coalescence. The increase in resistance in the later period resulted from the aging and degradation of PANI. Also the existence of oxygen showed great effect on the degradation of the film conductivity. The movable PS chain migrating in the film and aggregating on the surface seemed to have no direct relation to the transmitting path. The conductivity of the film was mainly controlled by PANI. Typically, the resistance of the film was about 6000 Ω /sq, and the conductivity was about 0.3 S/cm for film formed for around 10 min at 140°C.

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